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HYDROLYSIS METHOD

The present invention relates to a method, for the preparation of a fatty acid ester component, and a process, for the production of a sterol fatty acid ester-rich composition, according to what is defined in the preamble of appending independent claims. The present invention also relates to the use of said fatty acid ester component and said sterol fatty acid ester-rich composition and to products comprising said sterol fatty acid ester-rich composition.

The present invention particularly relates to a process for the production of a sterol fatty acid ester-rich composition by a catalytic esterification of a mixture comprising at least a sterol composition and a fatty acid glyceride composition. The present invention also relates to a method for preparation of a fatty acid ester component suitable for use in said process.

BACKGROUND

A high serum cholesterol value is believed to be one of the most significant single indicator of the risk of coronary disease. Serum cholesterol levels can be lowered by dietary means, by paying attention to the quantity and type of the oil or fat ingested and to the amount of cholesterol intake. It is known that ingested plant sterol lowers the level of serum cholesterol in human and animals. Studies have shown that orally administered plant sterols, such as sitosterol and its hydrogenated congener sitostanol, reduce serum total and low density lipoprotein (LDL) cholesterol levels by partly inhibiting the absorption of both dietary and biliary cholesterol from the intestines. Sitostanol is believed to be one of the most effective inhibitors of cholesterol absorption. The use of plant sterols in foods, particularly in so-called functional foods, as well as, in pharmaceutical and cosmetic products has therefore gained much interest.

Although both free crystalline plant sterols and their fatty acid esters can be utilised in these applications, the fatty acid esters are preferred for several reasons. Sterols have to be in a bioavailable form in order to be capable of inhibiting the absorption

of cholesterol. Various preparations of free plant sterols dissolves at different rates in the fat phase of the food digesta and will therefore affect cholesterol absorption with different efficacies.

5 Different food products can easily be enriched with a desired level of plant sterol in their fatty acid ester form without negative effects on the sensory properties of the products. Furthermore, the fat-like physical properties of sterol fatty acid esters makes it technically feasible to use them in the production of sterol enriched food products, irrespective of the food matrices used. By enriching the food product with
10 desired levels of plant sterol the cholesterol lowering effect of the food product can easily be optimised.

Various methods for esterifying sterols, as well as, stanols, the hydrogenated form thereof, have been proposed. Many of these utilise chemical reagents that cannot be accepted in the production of sterol fatty acid esters to be used in food applications. Such reagents may for instance include food grade incompatible moieties, such as
15 acid chlorides, anhydrides or organic solvents.

US 3 751 569 suggests adding plant sterol fatty acid esters in cooking oil with the objective of lowering the serum cholesterol levels in man. The sterol fatty acid ester is prepared by esterification of free sterols with fatty acid anhydride, with perchloric acid acting as catalyst. The catalyst and anhydride reagent cannot be accepted in a
20 food grade process.

GB 1 405 346 suggests conversion of free sterols in vegetable oil into their corresponding fatty acid esters, in order to produce a clear oil. Thereby a fatty acid ester of a monohydric aliphatic alcohol C1-4 is mixed to the oil. The fatty acid ester has been prepared in a separate process. The mixture of free sterols and fatty acid
25 ester is esterified in the oil at elevated temperature in the presence of e.g. an alkali metal alcoholate catalyst. Monohydric alcohol, such as methanol, is liberated and has to be continuously removed in order to accelerate the esterification reaction. This method uses an excess of fatty acid ester, and the method produces an interesterified oil containing sterol esters.

US 5 502 045 suggests the use of e.g. sitostanol fatty acid esters to lower cholesterol levels in serum. The esters can be used as such or they can be added to foods. The stanol fatty acid ester is prepared by an esterification technique of a mixture containing a free crystalline stanol component and a fatty acid ester, such as fatty acid methyl ester, or a fatty acid ester mixture component. A catalyst, such as Na-ethylate, is needed for the esterification reaction. The catalyst may be destroyed after the esterification by adding water to the mixture.

WO 02/055639 suggests a process for preparation of a fat composition containing sterol esters, prepared in a one pot direct esterification of sterol with triglyceride. Thereby at a high temperature a sterol raw material is mixed with and dissolved in a triglyceride. An alkaline catalyst is added and esterification is allowed to take place. The catalyst is neutralised by the addition of acid and the fat composition obtained is purified. The fat composition prepared does obviously besides sterol fatty acid ester include rather high amounts of other components, such as free sterol, unreacted triglycerides, diglycerides and monoglycerides.

WO 02/060916 suggests a method for the production of a sterol ester rich composition by esterification of sterols with fatty acyl glyceride from vegetable oil in the presence of an alkali catalyst. Following the esterification the reaction mixture is distilled to remove glycerol to enhance the formation of sterol esters. An acid is added to the reaction mixture to render the alkali catalyst inactive. Thereafter a sterol ester-rich fraction is isolated from the reaction mixture using organic solvents in combination with aqueous washes. In the reaction a significant stoichiometric excess of fatty acid acyl groups is needed in most cases. A complete, 100 %, product formation is not aimed at. The sterol ester-rich composition produced includes, besides sterol esters, considerable amounts of mono-, di- and triglycerides, as well as, free sterol.

The known methods for producing sterol fatty acid esters seem to lack in efficiency of the conversion processes. For optimal results more than stoichiometric amounts of fatty acid triglycerides or expensive pre-prepared fatty acid esters are used in the esterification process. In most processes a final product is achieved which contains

besides sterol fatty acid esters rather high amounts of unreacted components, such as mono-, di- and/or triglycerides, as well as, unreacted free sterols. These have to be removed in separate processes in order to get a pure sterol fatty acid ester. In some prior art processes reagents or catalysts are utilised that cannot be accepted in food preparing processes.

Due to the huge commercial interest in pure sterol fatty acid esters there are obvious needs for cost effective esterification processes that can be used to efficiently produce pure sterol fatty acid ester from vegetable oils or fats. Glycerol and catalyst should be easy to separate from the product. Also it should preferably be possible to carry out the process with existing equipment used for esterification of edible oils and fats.

SUMMARY OF THE INVENTION

The invention relates to a process for the production of a sterol fatty acid ester-rich composition. A sterol composition, a fatty acid glyceride composition and an esterification catalyst is combined to form a reaction mixture. Esterification of sterol(s) takes place in the mixture, providing sterol fatty acid ester(s), glycerol and glycerides. A hydrolysing and alkylating composition is added to the mixture to hydrolyse glycerides present therein to produce corresponding fatty acid alkyl ester(s) and glycerol. Glycerol is separated from the process. The sterol fatty acid ester containing mixture is purified by separating fatty acid alkyl ester therefrom, thereby providing a sterol fatty acid ester-rich composition. The fatty acid alkyl ester may be recycled into the esterification step in the beginning of the process.

It is an object of the present invention to provide an improved process, for the production of a sterol fatty acid ester-rich composition, in which method and process the above mentioned disadvantages have been minimised.

It is thereby an object of the present invention to provide an efficient process for the production of a sterol fatty acid ester rich composition, in which the content of free sterols, as well as, mono-, di- and triglycerides is minimised.

5

It is further an object of the present invention to provide an efficient process for the production of a sterol fatty acid ester-rich composition with a minimal, in practice stoichiometric or almost stoichiometric, glyceride feed.

It is furthermore an object of the present invention to provide a process for the
5 production of a sterol fatty acid ester-rich composition in which by-products and catalysts are separated easily from the sterol ester-rich composition.

It is still further an object of the present invention to provide an efficient and rapid process for the production of a sterol fatty acid ester-rich composition.

It is also an object of the present invention to provide an improved method, for the
10 preparation of a fatty acid alkyl ester component in a mixture comprising at least a glyceride component and a sterol fatty acid ester component, while preventing or minimising the hydrolysis of the sterol fatty acid ester component.

It is then also an object of the present invention to provide a process for the
15 production of a sterol fatty acid ester-rich composition, which process makes possible the preparation of a fatty acid alkyl ester component, participating in the sterol esterification, within the process itself.

It is additionally an object of the present invention to provide a process for the production of a sterol fatty acid ester-rich composition, in which reagents and catalysts are used, which are accepted in food grade processes.

20 It is still an object of the present invention to provide a process wherein there is no need to form an oil-water phase system, which would lead to increased losses of reactants and/or sterol fatty acid ester(s) because of emulsion formation.

In order to fulfil the above objects, a method and a process according to the present invention are characterised by what is disclosed in the characterising parts of the
25 appended independent claims.

A typical method for the hydrolysis of mono-, di- and/or triglycerides in a mixture containing besides the glycerides at least a sterol fatty acid ester component without significant hydrolysis of the sterol fatty acid ester(s) simultaneously

present in said mixture, is according to the present invention characterised by adding to said mixture

- a hydrolysis catalyst and
- an alkylating component,

- 5 said components providing for hydrolysis of mono-, di- and/or triglycerides and alkylation of liberated fatty acid components. These reactions take place in the mixture without significant hydrolysis of sterol fatty acid esters present.

The hydrolysis catalyst is typically chosen from the group of bases comprising alkali hydroxides, such as KOH and/or NaOH, and alkali oxides.

- 10 The alkylating component is typically chosen from the group of lower alcohols comprising C1-4 alkanols, preferably methanol and/or ethanol.

The starting mixture for the hydrolysis typically contains at most 50 %, typically 1-30 %, by weight glycerides and at least 50 %, typically 70-99 %, by weight sterol fatty acid ester component(s).

- 15 The reaction mixture typically contains 0,01-10 %, more typically 0,05-2 %, by weight of the hydrolysis catalyst.

The reaction mixture typically contains 0,01-75 %, more typically 0,1-40 %, most typically 0,5-30 %, by weight of the alkylating component

- 20 Typically the hydrolysis catalyst and the alkylating component are added to the mixture as a pre-prepared hydrolysing and alkylating composition. Preferably the hydrolysis catalyst is KOH and the alkylating component is methanol. More preferably these components are added as a pre-prepared methanolic KOH composition.

- 25 The hydrolysing and alkylating composition or its components typically comprise at least 50 % by weight methanol and at most 50 % by weight KOH, preferably 65-99,5 %, more preferably 80-99 %, most preferably 85-95 % by weight of methanol and preferably 0,5-35 %, more preferably 1-20 %, most preferably 5-15 % by weight of KOH.

The temperature of the mixture is preferably maintained at a temperature between 60-100 °C, more typically at a temperature between 60-80 °C, for 1 minute to 6 hours, typically 0,5-2 hours. The pressure is maintained at vacuum pressure of at most 100 kPa, typically at most 7 kPa.

- 5 A typical process utilising the present invention for the production of a sterol fatty acid ester-rich composition includes following two main reaction steps:
- a first step, including esterification of sterol components in a reaction mixture including glyceride and fatty acid alkyl ester components for the formation of sterol fatty acid ester(s), i.e. for the formation of one or more sterol fatty acid esters, and
 - 10 - a subsequent second step, including hydrolysis of glycerides still present in the reaction mixture and an esterification of fatty acid components thus formed for the formation of fatty acid alkyl ester(s), i.e. for the ester formation of one or more fatty acid with one or more alkyl, and
 - recycling of at least a portion of the fatty acid alkyl ester(s) formed into the
 - 15 reaction mixture in the first step

In the present description of the invention, as well as, in appending claims the term "sterol" means, unless otherwise stated, sterol and its hydrogenated congener stanol or a mixture of these. The term sterol includes in its broadest form, besides various plant sterols and plant stanols, also cholesterol, which is an animal sterol and which

20 may be used e.g. in cosmetic applications. Preferably the sterol composition used in the process is rich in sterol raw material selected from the group consisting of 4-desmethyl sterols, 4-desmethyl stanols, 4-monomethyl sterols, 4-monomethyl stanols, 4,4-dimethyl sterols and 4,4-dimethyl stanols and mixtures of these. Most typically 4-desmethyl sterols and/or 4-desmethyl stanols are used.

- 25 In the present description of the invention, as well as, in appending claims the term sterol fatty acid ester-rich composition, produced by the present new process, means, unless otherwise stated, a composition including at least 90 %, more typically at least 94 %, most typically at least 97 % by weight sterol fatty acid ester(s).

In the present description the term "esterification" of sterol components includes interesterification of sterol components with fatty acid components of glycerides present in the reaction mixture and/or transesterification of sterol components with fatty acid derivatives present in the reaction mixture.

5 DETAILED DESCRIPTION OF THE INVENTION

In a typical process, utilising the present invention, the first step, i.e. the first esterification step, will take place in a reaction mixture including the following components fed into a reaction vessel:

- a sterol composition, comprising one or more sterols;
- 10 - a glyceride composition, comprising one or more glycerol fatty acid esters of one to three same or different fatty acids and
- a fatty acid alkyl ester composition, comprising one or more fatty acid lower alkyl esters.

A typical mixture would include, in mol ratio, about 1 mol of sterol(s), about 0,3-0,7
15 mol of glyceride(s) and about 0,9-2,1 mol of (recycled) fatty acid alkyl ester(s).

As will be shown later, it may not always be necessary to include in the mixture, at the very initial starting phase of the process, a fatty acid alkyl ester composition. A stoichiometric excess of glyceride may compensate for the absence of the fatty acid
20 alkyl ester at the initial phase. In the continued run of the process fatty acid alkyl ester will be formed in the process itself and recycled to the beginning of the process to form the above mixture.

Typically the mixture is dried and the sterol components dissolved by increasing the temperature of the mixture. The pressure in the vessel may be decreased to enable separation of the water separated from the mixture. Alternatively or in addition, the
25 compositions of the mixture may be dried and dissolved separately before combining them into a mixture.

A catalyst, such as NaOCl is fed into the reaction vessel in order to bring about the first esterification reactions in the process, i.e. to bring about the esterification

reactions between sterol components present in the sterol composition and fatty acid components present in the glyceride and fatty acid alkyl ester compositions fed into the reaction vessel. Thus, in the esterification reactions of the first step, sterol fatty acid ester(s), partial glycerides and glycerol are formed.

- 5 After the esterification reactions, in the first step, have reached a desired conversion level, such as at least 90 %, typically at least 94 %, more typically at least 98 %, conversion, the thus reacted mixture typically contains, besides the sterol fatty acid ester(s) and glycerol formed, possible unreacted sterol components and partly and/or totally unreacted glycerides, i.e. mono-, di- and/or triglycerides, as well as, fatty acid
10 alkyl ester(s) and catalyst.

Thereafter in a typical process utilising the present invention, the second step, i.e. the hydrolysis of glycerides and the esterification of fatty acid components thus formed, will take place in the reacted mixture, in the same or another reaction vessel.

- 15 A hydrolysis catalyst, preferably an alkali catalyst, such as KOH or NaOH, is fed into the reacted mixture in order to bring about hydrolysis of glycerides therein.

In the second step, the hydrolysis catalyst itself, the amount of catalyst used and the reaction conditions, such as time and temperature, are chosen so as not to, at least not significantly, hydrolyse the sterol fatty acid ester(s) present in the reacted
20 mixture, while still hydrolysing the glycerides in a suitable manner. The conditions are chosen so as to achieve an as complete as possible hydrolysis of mono-, di- and triglycerides, while simultaneously avoiding formation of free sterols.

An alkylating component is fed into the reaction vessel in order to provide the alkyl component needed for the esterification, i.e. the alkylation, of fatty acid components
25 formed by the hydrolysis of glycerides. The alkylating component is preferably fed into the vessel simultaneously with the hydrolysis catalyst, the catalyst thereby typically being dissolved in the alkylating component. Typically the alkylating component is a lower alkyl alcohol, such as methanol or ethanol leading to methylation or ethylation of the fatty acid components.

Thus in the second step of the present process glycerides, present in the reacted mixture formed in the first step, are hydrolysed to form fatty acid components and glycerol. And the fatty acid components thus formed are esterified, in a second esterification reaction of the present new process, to form corresponding fatty acid alkyl ester(s).

Glycerol formed in the first esterification reactions and in the hydrolysis reactions is typically gathered as a separate glycerol phase at the bottom of the reaction vessel(s) and may then be easily removed therefrom. Catalyst(s) used in the esterification and hydrolysis processes, e.g. NaOCH_3 in the first step and KOH or NaOH in the second step, typically gathers in the glycerol phase and may be efficiently removed from the process together with the glycerol, e.g. by draining.

After the second esterification, i.e. the alkylation, reaction has reached a desired conversion level and the glycerol and the catalysts have been removed, the remaining mixture contains, besides the sterol fatty acid ester(s), mainly fatty acid alkyl ester(s), as well as, possibly, typically minor, amounts of unreacted reagents, intermediate products and impurities. The fatty acid alkyl ester and unreacted reagents, such as free sterols, may separately be separated, e.g. by distillation, from the produced sterol fatty acid ester containing mixture. The fatty acid alkyl ester is typically at least partly recycled to the beginning of the process, to be included in the reaction mixture.

The present invention utilises the finding that incompletely reacted mono and di glycerides, as well as, unreacted triglycerides, still present in the process after the first reaction step, i.e. after having reached the chosen conversion level of the first esterification reactions between sterol and glyceride components, may be hydrolysed in a second reaction step without significantly hydrolysing the sterol fatty acid ester(s) formed. Typically at most 20 %, more typically at most 10 %, most typically at most 5 % of the sterol fatty acid ester(s) are hydrolysed. Of the glycerides typically at least 90 %, more typically at least 95 %, most typically at least 98 % is hydrolysed. Hydrolysis of glycerides provides reactive fatty acids, which are simultaneously esterified with lower alcohols so as to form fatty acid alkyl esters

that may be recycled to the first reaction step to provide an excess of reactive fatty acid derivatives into the esterification of sterol(s). The excess of fatty acid ester(s) enables optimal conversion levels in the esterification of sterols even if only about a stoichiometric input of "virgin" or "new" fatty acid components, in glyceride form, is provided in a continuous process or repeated batch process.

The optimal conversion of sterol(s) minimises the free sterol content in the final sterol fatty acid ester product. The hydrolysis of glycerides, on the other hand, minimises the amount of mono-, di- and triglycerides in the final sterol fatty acid ester product. Thus a pure sterol fatty acid ester-rich product is achieved. The composition of the feed into the reactor vessel in the first step allows for high sterol conversion in relatively short reaction times.

Therefore in a continuous process or repeated batch process for the production of a sterol fatty acid ester-rich composition, according to the present invention, an input of only about stoichiometric amounts of sterol and glyceride is typically needed. Simultaneously fatty acid alkyl ester is preferably continuously recycled, as described above, within the process.

During normal steady state conditions normally no continuous input of external fatty acid alkyl ester is recommended. However, at the very initial stage of the process, i.e. before any fatty acid alkyl ester component has been formed in the process, a small input of separately prepared external fatty acid alkyl ester may be needed. Alternatively an excess of glyceride may be fed into the system during the initial stage of the process so as to provide an excess amount of fatty acid derivatives needed in the first esterification reactions and the glycerides needed in the hydrolysis/esterification reactions.

The process according to the invention may be performed as a batch process in one single vessel or in two or more consecutive vessels. Alternatively, the process may be performed as a continuous process.

Purification, such as bleaching and/or filtration, of the sterol fatty acid ester and fatty acid alkyl ester produced may be performed in any suitable manner known per se within the reaction vessel itself or in any separate equipment.

Preferably the purification of the sterol fatty acid ester containing mixture includes
5 bleaching, filtration and/or deodorisation.

The present new process may be applied in the esterification of a wide variety of sterols. Both plant sterols and animal sterols may be esterified to provide desired sterol fatty acid ester-rich compositions for use in food, pharmaceutical and cosmetic applications.

10 The sterol composition used in a process according to the present invention may thereby be obtained from one or more natural oils or fats, such as vegetable, fungal or animal oils or fats, or their mixtures. Typically sterol components obtained from the preparation processed of one or more of the following plant or vegetable oils or fats are used: tall oil, rapeseed oil, soy bean oil, wheat germ oil, rice bran oil, corn
15 fiber oil, sunflower oil, safflower oil, corn oil and olive oil.

The sterol composition used in the process typically includes one or more sterol components chosen from the group consisting of sitosterol, sitostanol, campesterol, campestanol, stigmasterol, brassicasterol, dihydrobrassicasterol, taraxasterol, clionasterol, cholesterol, suitable derivatives and reduction products of the
20 foregoing, and mixtures of these.

The present invention makes possible the use of a variety of fatty acid components, including particular fatty acid components that would not ordinarily be available as such on the market or, if available, would render a rather high price. These particular fatty acid components may, however, be present in glycerides available on
25 the market and thus available for the present process.

Glyceride compositions applicable in processes according to the present invention comprise a glycerol fatty acid ester of one to three same or different fatty acids. Typically the glyceride composition comprises a main triglyceride component and possible minor amounts of mono- and/or diglycerides.

The glyceride composition may comprise saturated and/or unsaturated C₄-C₂₈ fatty acid esters of glycerol, preferably C₁₆-C₂₂ fatty acid esters of glycerol, most preferably C₁₆-C₁₈ fatty acid esters of glycerol. The acids may be saturated or mono-, di or polyunsaturated.

- 5 The glyceride component may be selected from different types of glycerides, such as glycerides derived from plant, animal, synthetic or fungal oils or fats, such as vegetable oils and fish oils. The oils or fats may be partially or fully hydrogenated or may include a fatty acid with an otherwise modified composition.

- 10 Typically, however, a glyceride composition comprising one or more fatty acid glyceride components selected from a group of glycerides derivable from vegetable oils or fats is used. Thus glycerides of soybean, rapeseed, sunflower, corn, wheat, rice, safflower, olive, cottonseed, linseed, flaxseed, sesame, peanut, almond, palm and coconut oil or fat, and mixtures of these, may be used.

- 15 Various known suitable esterification catalysts may be used in the esterification of the sterol component. The esterification catalyst may preferably be chosen from the group comprising metal alkoxides, such as NaOCH₃ or NaOC₂H₅, alkali hydroxides, metal oxides, metal soaps, metal alloys, metal hydrides, metal amides and/or their mixtures. The amount of catalyst needed in the esterification reactions depends on the catalyst composition, as well as, on process conditions. Sodium
- 20 methoxide, i.e. NaOCH₃, has proven a very suitable catalyst. Typically an amount of about 0,3-1 % by weight, more typically 0,5-0,8 % by weight NaOCH₃ catalyst calculated on the amount of sterol is needed for a good esterification result. The catalyst may be introduced into the reaction vessel together with the sterol composition and/or the glyceride composition, or it may be introduced into the
- 25 vessel separately. Sodium methoxide can easily be removed from the process together with glycerol.

- Various known hydrolysis catalysts may be used to activate the hydrolysis of glycerides in the second step of the present process. By choice of catalyst and process conditions, care should, however, be taken not to activate a hydrolysis of
- 30 sterol fatty acid esters also present in the reacted mixture. Different bases, such as

alkali hydroxides or alkali oxides may be used. Advantageously KOH and/or NaOH, preferably KOH is used to activate the hydrolysis.

About 0,01-10 % by weight of hydrolysis catalyst calculated on the amount of reaction mixture is typically needed to activate the hydrolysis properly.

- 5 Preferably 0,05-2 % hydrolysis catalyst is used.

- An alkylating component is added to the reacted mixture to esterify the fatty acid(s) formed by the hydrolysis. The alkylating component is preferably a lower alcohol (e.g. C1-4 alkanol), more preferably methanol or ethanol, most typically methanol. The hydrolysis catalyst is typically dissolved in the alkylating component before
10 adding the catalyst and the alkylating component as a combined hydrolysating and alkylating composition into the reacted mixture from the first step.

About 0,01-75 % by weight of alkylating component calculated on the reaction mixture is typically added to facilitate the alkylation. Preferably the added amount is 0,1-30 %, more preferably 0,5-30 %.

- 15 A combined hydrolysating and alkylating composition, comprising KOH and methanol typically includes at least 50 % by weight methanol and at most 50 % by weight KOH, preferably 65-99,5 %, more preferably 80-99 %, most preferably 85-95 % by weight of methanol and preferably 0,5-35 %, more preferably 1-20 %, most preferably 5-15 % by weight of KOH. These components may also be added
20 separately in corresponding amounts.

Preferably the hydrolysis catalyst and the alkylating component are added to the sterol fatty acid ester containing mixture when the esterification reactions of the first reaction step are complete or mainly complete.

- Process conditions, such as temperature, vacuum, pressure and/or time, may be used
25 to control the reactions taking place in the first and second process steps.

Before the actual esterification reactions take place between the sterol component(s) and glyceride component(s) the reagents are preferably dried at high temperature and under vacuum. The temperature of the components is typically elevated to

above 100°C, typically to between 110-130°C. Preferably a vacuum of less than 7 kPa is used to remove water.

- The actual esterification between sterol and glyceride/fatty acid alkyl ester components is typically performed at high temperature and under vacuum. The temperature is kept between 100-200 °C, typically between 100-160 °C, more typically between 115-145 °C. Vacuum level is kept between 2-100 kPa, typically below 7 kPa. Esterification normally takes about 0,1-10 hours, typically 1-3 hours, most typically about 2 hours, depending on reagents and catalyst used, as well as, on temperature, vacuum levels and desired level of reaction conversion.
- 10 The hydrolysis of glycerides is performed at a temperature, which typically is lower than the above mentioned esterification temperatures, typically between 60-110 °C, more typically between 60-80°C. The hydrolysis is maintained for 1 minute to 6 hours, typically 0,5-2 hours. Hydrolysis at 80 °C may thus be continued for 0,1-2 hours, typically 30 minutes.
- 15 After hydrolysis and alkylation the fatty acid alkyl ester formed may be separated from the sterol fatty acid ester-containing mixture in a so-called deodorisation stage, by distillation. The fatty acid alkyl ester is thereby typically separated from the sterol ester by high vacuum stripping at temperatures between 160-240 °C. The process may take from a few minutes to a few hours, depending on process conditions.
- 20 The present invention will be more readily understood from the following description of an exemplary process utilising the present invention, as shown in Figure 1 schematically showing the process steps. The consecutive process steps may be performed in distinctly separate reaction vessels or in a single elongated vessel being divided in consecutive separate reaction zones, still allowing a reaction
- 25 mixture to flow through the vessel. The figure depicts a batch process.

An external feed of a glyceride composition, such as a refined bleached and deodorised triglyceride, and a sterol composition, such as a sterol rich in 4-des-methyl sterols, as well as, a recycled feed of fatty acid alkyl ester FaMe is fed into the first stage, Step 1, to form a mixture therein. A first catalyst, Catalyst 1, such as

NaOCH₃, is fed into the mixture and the mixture temperature is raised to the reaction temperature level to start esterification of the sterol composition.

Esterification reactions result in the formation of sterol fatty acid ester(s), i.e. the Sterol-ester product, and glycerol, as well as, some only partly reacted mono- and diglycerides and methanol. Thus a reacted mixture moving from Step 1 to the second stage, Step 2, will normally contain besides significant amounts of sterol fatty acid esters and glycerol formed and possible minor amounts of unreacted free sterols and triglycerides, some partly reacted mono- and diglycerides. The methanol is removed by vacuum. The removed methanol may also be reused by recycling it into the second stage of the process.

In the second stage, Step 2, a second catalyst, Catalyst 2, including a hydrolysis catalyst, such as KOH, and an alkylating component, such as methanol, is added to the reacted mixture and the temperature of the reacted mixture is set to the second reaction temperature level to start hydrolysis and alkylation. In Step 2 mono-, di- and triglycerides in the reacted mixture are hydrolysed to form fatty acids and more glycerol. Glycerol, which contains catalyst residue, as well as, other impurities, may be continuously drained from Step 2 to enhance reactions. The free fatty acids formed react with the alkylating component, which results in the formation of fatty acid alkyl esters.

From Step 2 the reacted mixture, now mainly containing sterol fatty acid ester(s) and fatty acid alkyl ester(s), is conveyed to purification treatment(s) considered necessary in each particular case. The purification may include, as shown in the figure, a bleaching step 10, a filtration step 14 and a deodorisation step 16, known per se. All these steps may not always be necessary. In some applications other cleaning steps known per se may be used. The cleaning steps may need the addition of some cleaning aid, such as adsorbent 12 added into the mixture in the bleaching step 10.

The deodorisation step 16 may include distillation or stripping of fatty acid alkyl ester at 160-240 °C from the sterol fatty acid ester to form a sterol fatty acid ester-rich composition, which contains a high amount of sterol ester(s), typically at least

90 %, more typically at least 94 %, most typically at least 97 % by weight sterol fatty acid ester(s) and a low amount of free sterol(s), typically at most 10 %, more typically at most 6 %, most typically at most 3 % by weight free sterols. The composition contains a low amount of total glycerides, typically less than 2 % triglycerides, more typically less than 1 % by weight triglycerides.

The present invention will be more readily understood from the following examples. The examples are intended to illustrate the present invention, not to limit the invention. In this specification unless otherwise stated the percentages are given as % by weight.

10

EXAMPLE 1

Stanol fatty acid esters were prepared in laboratory scale by carrying out esterification reactions in a mixture comprising rapeseed oil, plant stanol and rapeseed oil-based methyl ester.

- 15 Plant stanol, having a composition of 68.2 % sitostanol, 28.3 % campestanol, 1.1 % sitosterol and trace amounts of unsaturated sterols, was prepared by hydrogenation of commercially available plant sterol. One mol of the thus prepared plant stanol was mixed with 0.33 mol of rapeseed oil and 1 mol of rapeseed oil-based methyl ester. The mixture was dried at 110-120°C and at vacuum below 7 kPa.
- 20 The temperature of the thus dried mixture was reduced to 90-95 °C. Sodium methoxide catalyst in an amount of 0.8 % by weight of total sterol/stanol, was added to the mixture. The temperature of the thus formed reaction mixture was increased to 120 °C and the esterification was carried out under vacuum for a relatively short period, i.e. for 2 hours. The conversion, of stanol and glyceride to stanol fatty acid ester and glycerol in the presence of excess fatty acid methyl ester, was monitored
- 25 by gas chromatographic (GC) analysis. Once final (> 90 %) conversion was achieved, the temperature was reduced to 80 °C (product of Step 1).

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Thereafter 5 % by weight of a catalyst, including 11 g KOH in 89 g methanol, was added to the esterified reaction mixture to hydrolyse glycerides, i.e. tri-, di- and monoglycerides, still present in the mixture and form fatty acid methyl esters and more glycerol.

- 5 Glycerol and catalyst residues settled on the bottom of the reactor were decanted out of the reactor. After hydrolysis of glycerides and catalyst removal, the mixture was dried at 95 °C under vacuum. The thus dried material was bleached using 1 % by weight adsorbing aid (Trisyl®, Grace, Germany) for 20 minutes at 95 °C and vacuum below 7 kPa, for removing catalyst residues, metal and color compounds.
- 10 After removal, by filtration, of the adsorbing aid, standard laboratory scale evaporation, in a thin film evaporator, was carried out to remove the excess of fatty acid methyl esters and provide a stanol fatty acid ester-rich product. The fatty acid methyl ester distillate was to be recycled and reused as raw material in the process. The concentrations of obtained stanol fatty acid ester, free stanol, glycerides and
- 15 fatty acid methyl ester were analysed in the intermediate product after Step 1 and in the stanol fatty acid ester-rich product.

The results were:

	Analysis	product of Step 1	purified product
		% by weight	% by weight
20	Free sterols/stanols	1.7	4.8
	Stanol fatty acid esters	66.3	94.6
	Monoglycerides	-	-
	Diglycerides	10.2	-
	Triglycerides	14.3	< 0.5
25	Free fatty acid methyl ester	7.5	

The results show approximately 25 % unreacted glycerides in the intermediate product but only traces in the final product.

EXAMPLE 2

Two test runs for the preparation, in laboratory scale, of a stanol fatty acid ester-rich product were performed. Thereby in a reaction vessel a reaction mixture, containing 0,33 mol rapeseed oil (RO), 1 mol stanol (STA) and 1 mol rapeseed oil-based methyl ester (ROME), was mixed with 0,6-0,8 % by weight NaOCH₃ catalyst
 5 calculated on the amount of stanol. The reaction mixture was esterified.

Thereafter the mixture was hydrolysed and alkylated by adding into the reaction vessel 5 % by weight of a hydrolysing and alkylating composition, comprising 89 % methanol and 11 % KOH. The hydrolysalation, which took place at atmospheric
 10 pressure and 80°C, took approx. 30 minutes. Glycerol phase formed settled at the bottom of the reaction vessel and was removed. Fatty acid methyl ester (FaMe) was distilled from the mixture. Fatty acid methyl ester thus separated from the mixture in the first test run was recycled and used as the fatty acid methyl ester feed (FaMe) instead of rapeseed oil (ROME) in the second test run. Otherwise the second run was
 15 performed in the same way as the first run. The stanol fatty acid ester (STAEST) yield was measured.

Results		First run	Second run
20	Feed STA	g	199
	Feed RO	g	146
	Feed ROME	g	148
	Feed FaMe	g	148
25	Catalyst NaOCH ₃	g	1.5
	Methanol + KOH	g	25
	Glycerol denanted	g	42
	FaMe distillate	g	153
	STAEST	g	297
			279

The stanol fatty acid ester-rich product produced was analysed. The results:

Analysis	First run % by weight	Second run % by weight
Free sterols/stanols	1.8	5.4
Sterol fatty acid esters	94.6	94.0
5 Monoglycerides	-	-
Diglycerides	-	-
Triglycerides	< 0.5	< 0.5

The examples illustrate non-continuous processes. The process may, however,
 10 easily be utilised in a continuous process. Only a feed of a batch of fatty acid methyl ester or excess glyceride seems to be necessary at the beginning of the process. It is also believed that in the process the quality of the recycled fatty acid methyl ester remains good, due to the renewing effect of the process.

The present invention provides a simple and cost-effective food grade process for
 15 the esterification of sterol compositions with glyceride compositions to provide a sterol fatty acid ester-rich composition, in which the content of free sterols, as well as, mono-, di- and triglycerides is minimised. Thus the present invention makes possible a surprisingly efficient use of fatty acid components present in glycerides, a minimised, in practice, about stoichiometric, glyceride feed is sufficient. The present
 20 invention also makes possible the use of a variety of fatty acid components, e.g. fatty acid components which would not ordinarily be available as such on the market or, if available, would render a rather high price, but which are present in glycerides available on the market. In a process utilising the present invention, there is no need to purchase or separately prepare the fatty acid or fatty acid alkyl ester
 25 components needed, as fatty acid alkyl ester components needed in the process may be derived from corresponding glyceride compositions introduced.

In a process utilising the present invention catalysts used in the esterification reactions gather in the glycerol phase and are thereby easily removed from the process. In prior known processes, on the other hand, catalysts have been inactivated
 30 by washing the reaction mixture with water. Such water treatment tends to cause emulsification of process liquids leading to various process problems. These problems are avoided in the new process.

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Claims

1. A method for hydrolysatation of mono-, di- and/or triglycerides in a mixture containing besides said glycerides at least a sterol fatty acid ester component, characterised by
5 adding to said mixture
 - a hydrolysatation catalyst and
 - an alkylating component, andproviding for hydrolysatation and alkylation reactions to take place in the mixture, without significant hydrolysatation of sterol fatty acid ester(s) present in the
10 mixture.
2. The method according to claim 1, characterised by the hydrolysatation catalyst being chosen from the group of bases comprising alkali hydroxides, such as K.OH and/or NaOH, and alkali oxides.
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3. The method according to claim 1 or 2, characterised by the alkylating component being chosen from the group of lower alcohols comprising C1-4 alkanols, preferably methanol and/or ethanol.
- 20 4. The method according to any one of claims 1 to 3, characterised by the mixture, before adding the hydrolysatation catalyst and the alkylating component, containing at most 50 %, typically 1-30 %, by weight glycerides and at least 50 %, typically 70-99 %, by weight sterol fatty acid ester component(s).
- 25 5. A process for the production of a sterol fatty acid ester-rich composition comprising the steps of:
 - (a) combining
 - a sterol composition, comprising one or more sterols,
 - a fatty acid glyceride composition, comprising fatty acid esters of one or more
30 fatty acids, and
 - an esterification catalyst to form a reaction mixture,

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- (b) performing esterification of sterol(s) in said reaction mixture to produce a sterol fatty acid ester containing mixture,
- (c) adding a hydrolysis catalyst and an alkylating component to hydrolyse mono-, di- and/or triglycerides present therein and to produce corresponding fatty acid alkyl ester(s) and glycerol, and
- (d) purifying the sterol fatty acid ester containing mixture to form a sterol fatty acid ester-rich composition.
6. The process according to claim 6, wherein to the reaction mixture or to its components in step (a) is added at least one fatty acid alkyl ester.
7. The process according to claim 5 or 6, wherein step (d) includes step (d1) comprising purifying said sterol fatty acid ester containing mixture by removing glycerol from said mixture.
8. The process according to claim 7, wherein in step (d1) the esterification catalyst and/or the hydrolysis catalyst is removed from the sterol fatty acid ester containing mixture together with glycerol.
9. The process according to any one of claims 5 to 8, wherein step (d) includes step (d2) comprising purifying said sterol fatty acid ester containing mixture by separating fatty acid alkyl ester from said mixture.
10. The process according to claim 9, comprising a further step of feeding fatty acid alkyl ester separated in step (d2) into the sterol composition, the fatty acid glyceride composition, the esterification catalyst and/or into the reaction mixture formed in step (a).
11. The use of a sterol fatty acid ester-rich composition produced by the process of any of claims 5 to 10 as a dietary, pharmaceutical and/or cosmetic product or in the preparation thereof.

12. A sterol fatty acid ester-rich composition produced by the process of any of claims 5 to 10.
13. A fatty acid alkyl ester product produced by the method of any of claims 1 to 4.

L 3

Summary

The invention relates to a process for the production of a sterol ester-rich composition. A sterol composition, a glyceride composition, a fatty acid alkyl ester and an esterification catalyst are combined to form a reaction mixture. Esterification of sterol(s) takes place in the mixture, providing sterol ester(s). The new process is rapid and has a high level of conversion.

L 4

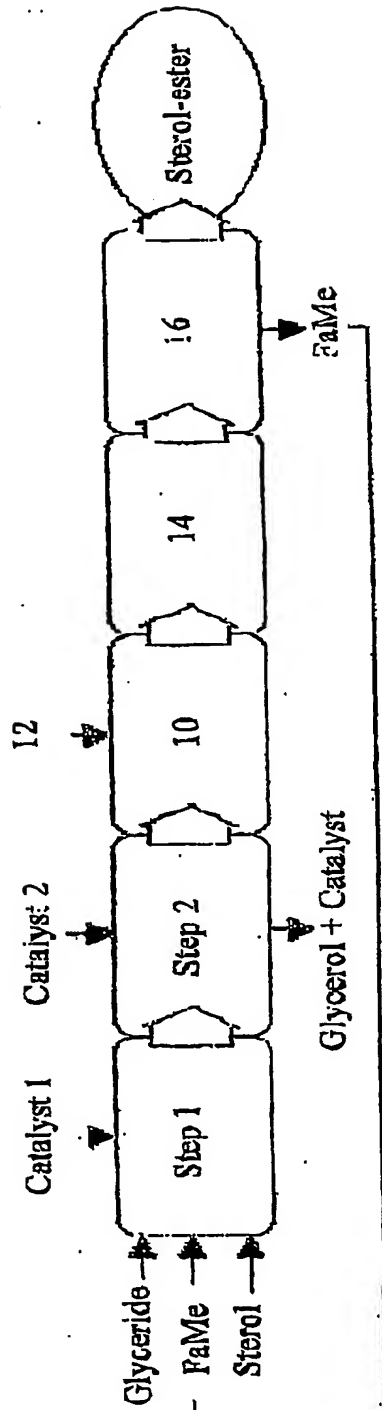


Figure 1

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